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Crystal and Molecular Structure of Tetra-*n*-butylammonium Di-μ-sulfido-bis(oxo-1,1-dicyanoethylene-2,2-dithiolatomolybdate(V)), $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$

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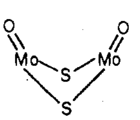
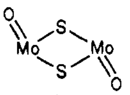
The crystal and molecular structure of tetra-*n*-butylammonium di-μ-sulfido-bis(oxo-1,1-dicyanoethylene-2,2-dithiolatomolybdate(V)), $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$, has been determined from three-dimensional x-ray diffraction data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 16.696$ (4), $b = 13.370$ (7), and $c = 13.265$ (7) Å, with $\alpha = 78.85$ (4), $\beta = 109.08$ (3), and $\gamma = 123.43$ (3)°. The calculated and observed densities are 1.30 and 1.28 (1), g cm^{-3}, respectively. Blocked-matrix, least-squares refinement has resulted in $R = 0.054$ for the 3933 data with $F_o^2 \geq 3\sigma(F_o^2)$. The anion has effective $mm\text{-}C_{2v}$ symmetry and contains an $Mo_2O_2S_2^{2+}$ core with cis-bent geometry and two S_b bridging atoms. The Mo···Mo distance is 2.821 (2) Å and the dihedral angle between the two $Mo(S_b)_2$ planes is 153.1°. Each Mo atom possesses distorted square-pyramidal coordination geometry with the two S_b atoms and two S_l atoms from an $[S_2C_2(CN)_2]^{2-}$ ligand forming the basal plane and an O atom in the axial position. The Mo–O distances for the two Mo atoms are not significantly different (1.661 (7) and 1.667 (7) Å). The average Mo–S_b distance is 2.300 (4) Å, and the average Mo–S_l distance is 2.434 (3) Å. It is proposed that the steric requirements of the coordinating ligands determine whether an $Mo_2O_2S_2^{2+}$ core adopts cis-bent or trans-planar geometry.

Introduction

Recent studies of the chemistry of sulfido complexes of molybdenum have been stimulated by the general interest in polynuclear metal compounds[1,2] and by the proposal[3,4] that sulfur is a donor atom in molybdenum-containing enzymes, especially xanthine oxidase. The existence of stable di-μ-sulfido-bis(oxomolybdenum) complexes is now well established[1,5–8] and two distinct geometries are known for the $Mo_2O_2S_2^{2+}$ core. Complexes of cysteine,[5,7] histidine,[6] and EDTA[8] contain a cis-bent core (**1a**) with a dihedral angle between the two MoS_2 planes of ~150°, whereas the cyclopentadienyl compound[1] has a trans-planar core (1b). Surprisingly, no structures have been reported for complexes of the $Mo_2O_2S_2^{2+}$ core with ligands containing only sulfur donor atoms.[9] The paucity of accurate structural data for dimeric molybdenum complexes of ligands with sulfur donor atoms and the existence of two geometries for the $Mo_2O_2S_2^{2+}$ core prompted the present determination of the structure of tetra-*n*-butylammonium di-μ-sulfido-bis(oxo-1,1-dicyanoethylene-2,2-dithiolatomolybdate(V)), $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$ (I).



1a



1b

Experimental Section

Very fine yellow air-stable crystals of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$ were prepared by Dr. J. McDonald and provided by Dr. William E. Newton. Crystals suitable for diffraction studies were grown as long plates by slow evaporation of a saturated 2:1 solution of acetone–ethanol. A crystal that exhibited sharp extinction under polarized light was selected for preliminary x-ray photographs using a precession camera and Mo Kα radiation. A systematic search of reciprocal space revealed no symmetry elements and suggested space groups $P1$ or $P\bar{1}$. Space group $P\bar{1}$ was assumed and confirmed by successful refinement of the structure.

Unit cell constants were determined from a least-squares refinement of the setting angles of 20 reflections which had been centered automatically on a Picker FACS-I diffractometer using Mo K$\bar{\alpha}$ radiation (λ 0.710 69 Å). The dimensions of the working cell are $a = 16.696$ (4), $b = 13.370$ (7), and $c = 13.265$ (7) Å, with $\alpha = 78.85$ (4), $\beta = 109.08$ (3), and $\gamma = 123.43$ (3)°. A Delauney cell reduction[10] yielded no additional symmetry. The dimensions of the reduced cell are $a = 16.620$, $b = 13.370$, and $c = 13.265$ Å, with $\alpha = 101.15$, $\beta = 99.95$, and $\gamma = 123.43$°. The reduced cell is related to the working cell by $a_r = a_w - b_w$, $b_r = -b_w$, and $c_r = c_w$. All computations and results are based upon the working cell. The experimental density of 1.28 (1) g cm^{-3} obtained by flotation in an aqueous KI solution requires two formula units of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(S_2C_2(CN)_2)_2]$ per cell. The calculated density is 1.30 g cm^{-3}.

Single-crystal diffraction data were collected from a crystal of dimensions 0.127 × 0.127 × 0.019 mm using graphite-monochromatized Mo Kα radiation, the θ–2θ scan technique, and a takeoff angle of 1.9°. The scan rate was 1°/min and 10-s backgrounds were taken at each end of the scans. The scan range was $2\theta_{MoK\alpha_1} - 0.7°$ to $2\theta_{MoK\alpha_2} + 0.7°$. Three standard reflections were checked every 100 reflections, and their intensities did not change significantly during data collection. A total of 7037 independent reflections with $3° < 2\theta < 50°$ were collected and reduced to F^2 and $\sigma(F^2)$ as described previously.[11,12] The factor p introduced to prevent overweighting of strong reflections was set at 0.04. Of the 7037 reflections, 3933 had $F_o^2 \geq 3\sigma(F_o^2)$. The absorption coefficient for the compound for Mo Kα radiation is only 7.0 cm^{-1}, and consequently no absorption correction was needed for the crystal used for data collection.

Table I. Final Atomic Parameters for $[Mo_2O_2S_2(S_2C_4N_2)_2]^{2-}$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mo1	-.30531(7)	-.13650(7)	.20296(8)	81.9(7)	73.1(7)	96.4(8)	22.8(5)	46.1(6)	-.7(6)
Mo2	-.20011(7)	-.21481(7)	.12141(8)	79.2(7)	63.7(6)	96.6(8)	19.5(5)	46.2(6)	1.8(6)
S1	.3446(2)	.2745(2)	-.1057(2)	71(2)	116(3)	90(2)	32(2)	17(2)	-25(2)
S2	.1570(2)	.1151(2)	-.2603(3)	79(2)	105(3)	185(4)	-19(2)	72(2)	-66(3)
S3	.2080(2)	.3904(2)	-.0883(2)	57(2)	77(2)	129(3)	17(1)	16(2)	-26(2)
S4	.0609(2)	.2629(2)	-.2105(2)	62(2)	110(3)	127(3)	6(2)	30(2)	-44(2)
S5	.4331(2)	.2241(2)	-.2609(2)	62(2)	105(2)	93(2)	10(2)	22(2)	-25(2)
S6	.2831(2)	.1037(3)	-.3853(3)	66(2)	162(3)	130(3)	-19(2)	47(2)	-67(3)
C1	.0979(7)	.3742(7)	-.1509(8)	65(7)	64(7)	87(9)	14(5)	28(6)	4(6)
C2	.0485(8)	.4421(8)	-.1533(10)	62(7)	61(8)	146(12)	10(6)	30(8)	-4(8)
C3	.0850(9)	.5286(11)	-.0987(17)	67(9)	101(12)	364(28)	21(8)	28(12)	-96(15)
C4	.0411(10)	-.4233(9)	.2091(11)	77(9)	74(9)	141(14)	20(8)	30(9)	24(9)
C5	.3884(6)	.1652(8)	-.3748(8)	56(6)	96(8)	86(8)	9(5)	21(6)	-16(7)
C6	.4308(8)	.1676(10)	-.4481(9)	68(8)	139(12)	92(10)	-8(8)	32(7)	-33(9)
C7	.5170(9)	.2205(10)	-.4337(9)	76(8)	124(12)	92(10)	2(8)	37(8)	-10(8)
C8	.3873(11)	.1224(17)	.4594(14)	89(12)	403(29)	187(18)	-75(15)	88(13)	-182(20)
O1	.3306(6)	.0299(6)	-.1231(7)	177(8)	111(7)	178(9)	78(6)	124(8)	50(6)
O2	.1887(6)	.1395(6)	-.0092(6)	172(8)	112(7)	155(8)	82(6)	119(7)	55(6)
N1	.1151(10)	.5992(13)	-.0564(21)	96(11)	188(17)	730(48)	32(11)	36(17)	-256(24)
N2	.1125(8)	-.4079(9)	.2564(10)	74(7)	149(11)	162(13)	29(8)	16(8)	38(9)
N3	.5860(8)	.2604(9)	-.4237(9)	82(7)	158(11)	155(12)	-11(8)	56(8)	20(9)
N4	.3535(11)	.0862(18)	.3809(15)	154(13)	636(37)	317(23)	-145(17)	139(15)	-362(26)

Table II. Final Atomic Parameters for the $[NC_{16}H_{36}]^+$ Ions

Atom	x	y	z	B
N5	.2622(4)	-.4877(5)	-.4244(5)	5.8(1)
C9	.1851(8)	-.5742(9)	-.4174(9)	7.7(3)
C10	.1029(9)	-.5655(11)	-.5090(11)	9.7(4)
C11	.0370(11)	-.6700(14)	-.5155(13)	12.6(5)
C12	.0572(12)	-.7529(15)	-.5550(14)	13.8(5)
C13	.2446(8)	-.3813(9)	-.4360(9)	7.2(3)
C14	.2214(9)	-.3538(10)	-.3471(10)	8.7(3)
C15	.2102(9)	-.2406(11)	-.3660(12)	10.0(4)
C16	.1884(12)	-.2075(14)	-.2772(14)	13.1(5)
C17	.2886(7)	-.4906(9)	-.5216(9)	7.2(3)
C18	.3166(10)	-.5866(12)	-.5259(12)	10.8(4)
C19	.3359(13)	-.5841(14)	-.6328(16)	13.7(5)
C20	.2605(14)	-.6003(16)	-.7246(18)	15.9(6)
C21	.3344(8)	-.5074(9)	-.3222(9)	7.3(3)
C22	.4167(9)	-.4256(11)	-.3059(11)	9.5(4)
C23	.4830(10)	-.4563(12)	-.1998(12)	10.4(4)
C24	.5562(11)	-.3741(13)	-.1669(13)	12.0(5)
N6	.2471(5)	-.1245(6)	.1329(6)	5.1(2)
C25	.2779(7)	-.2217(8)	.1372(8)	5.7(2)
C26	.3168(7)	-.2255(9)	.0510(9)	7.0(3)
C27	.3446(8)	-.3298(10)	.0647(10)	8.3(3)
C28	.3874(9)	-.3351(11)	-.0179(11)	10.0(4)
C29	.2171(6)	-.1371(8)	.2315(8)	5.6(2)
C30	.1715(7)	-.0558(8)	.2393(9)	6.9(3)
C31	.1514(8)	-.0781(9)	.3472(10)	8.0(3)
C32	.1040(9)	.0014(11)	.3583(11)	9.9(4)
C33	.1731(6)	-.1099(7)	.0318(7)	5.2(2)
C34	.0924(7)	-.1913(8)	.0188(8)	6.0(2)
C35	.0255(9)	-.1641(10)	-.0876(11)	8.9(3)
C36	-.0595(9)	-.2410(11)	-.1131(11)	9.8(4)
C37	.3178(6)	-.0282(7)	.1281(8)	5.5(2)
C38	.4025(7)	-.0285(8)	.2142(8)	6.3(2)
C39	.4626(11)	.0758(12)	.1866(13)	11.0(4)
C40	.4547(15)	-.0914(17)	-.2760(18)	16.6(7)

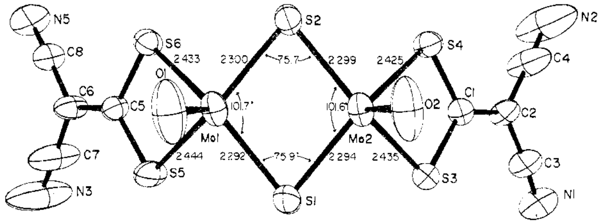


Figure 1. Perspective view of the $[Mo_2O_2S_2(i\text{-mnt})_2]^{2-}$ ion along the approximate C_2 axis.

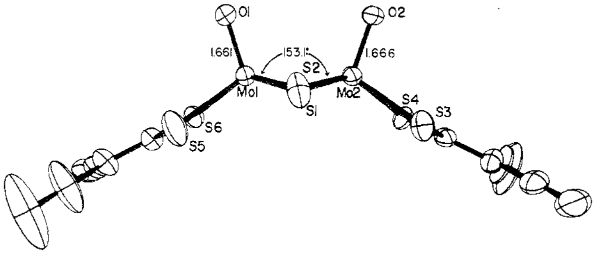


Figure 2. Perspective view of the $[Mo_2O_2S_2(i\text{-mnt})_2]^{2-}$ ion along the $S_1\cdots S_2$ vector.

Table III. Bond Distances (Å) in $[Mo_2O_2S_2(S_2C_4N_2)_2]^{2-}$

Mo1-Mo2	2.821 (2)	C1-S4	1.70 (1)
Mo1-S1	2.292 (3)	C1-S3	1.73 (1)
Mo1-S2	2.300 (4)	C1-C2	1.36 (1)
Mo2-S1	2.294 (3)	C5-C6	1.37 (1)
Mo2-S2	2.299 (3)	C2-C4	1.42 (2)
Mo1-O1	1.661 (7)	C2-C3	1.38 (2)
Mo1-O2	1.666 (7)	C6-C8	1.37 (2)
Mo1-S5	2.444 (3)	C6-C7	1.40 (2)
Mo1-S6	2.433 (3)	C4-N2	1.14 (1)
Mo2-S3	2.435 (3)	C3-N1	1.11 (2)
Mo2-S4	2.425 (3)	C8-N4	1.15 (2)
C5-S6	1.71 (1)	N3-C7	1.12 (1)
C5-S5	1.70 (1)		

The positions of the Mo atoms were determined from a three-dimensional Patterson function and the positions of the remaining nonhydrogen atoms were determined from a series of least-squares refinements and difference electron density maps. Refinement was based on F_o, with $\sum w(|F_o| - |F_c|)^2$ being minimized. The weights were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors tabulated by Ibers[13] were used for neutral S, O, N, C, and H, while those for Mo were obtained from Cromer and Mann.[14] The effects of both the real and imaginary anomalous scattering for Mo and S were included in the calculated structure factors using the anomalous scattering factors of Cromer and Waber.[15] Isotropic refinement of all atoms gave $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.140$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.168$ for the 3983 data with $F_o^2 \geq 3\sigma(F_o^2)$.

Limitations of core memory precluded full-matrix anisotropic refinement of the entire structure. Therefore, in subsequent cycles the anion and cations were refined as separate blocks with the scale factor common to both blocks. The anion was refined with all atoms anisotropic and the tetra-*n*-butylammonium cations were refined with all atoms isotropic. Two cycles of refinement on both the cation and anion gave $R_1 = 0.063$ and $R_2 = 0.081$. Idealized positions were determined for the 48 methylene hydrogen atoms, and their calculated structure factors were added as fixed contributions in the remaining refinements (C–H = 0.95 Å)[16]. The isotropic temperature factor for each hydrogen was assumed to be one unit larger than the carbon to which it was bonded. The contributions of the H atoms on the methyl carbons were ignored. Two more cycles of refinement on the cation and one more on the anion resulted in the final values of $R_1 = 0.054$ and $R_2 = 0.058$. The largest peak in the final difference map was 0.68 e Å^{-3}.

The final atomic parameters and estimated standard deviations for the anion and the cations are given in Tables I and II, respectively. A list of $10|F_o|$ and $10|F_c|$ is available (supplementary material).

Description and Discussion

The numbering scheme and perspective views of the $[Mo_2O_2S_2(S_2C_2(CN)_2)_2]^{2-}$ anion are shown in Figures 1 and 2. Important interatomic bond lengths and bond angles computed from the final atomic parameters are shown in Tables III–VI and in Figures 1 and 2. The estimated standard deviations for the bond lengths and angles were obtained from the inverse matrix of the final refinement of each block.

Each molybdenum atom is coordinated by two bridging sulfur atoms, two sulfur atoms of a 1,1-dicyanoethylene-2,2-dithiolate (*i*-mnt) ligand, and a terminal oxygen atom (Figures 1 and 2). The geometry of the dimer can best be described as two distorted square pyramids sharing the edge formed by the two bridging sulfur atoms. The anion has effective C_{2v}-*mm* symmetry, although no symmetry is imposed by the space group. Each molybdenum is displaced 0.72 Å out of the least-squares plane defined by the four coordinated sulfur atoms (Table VII). Recently two other five-coordinate square pyramidal molybdenum(V) dimers with approximate

Table IV. Bond Angles (deg) in $[Mo_2O_2S_2(S_2C_4N_2)_2]^{2-}$

S1-Mo1-S2	101.7 (1)	S5-C5-S6	110.6 (6)
S1-Mo2-S2	101.6 (1)	S3-C1-S4	110.3 (6)
S1-Mo1-S5	83.2 (1)	S5-C5-C6	124.3 (8)
S2-Mo1-S6	82.5 (1)	S6-C5-C6	125.1 (8)
S1-Mo2-S3	83.5 (1)	S3-C1-C2	124.5 (8)
S2-Mo2-S4	82.5 (1)	S4-C1-C2	125.2 (9)
Mo1-S1-Mo2	75.9 (1)	C5-C6-C8	120 (1)
Mo1-S2-Mo2	75.7 (1)	C5-C6-C7	121 (1)
S5-Mo1-S6	70.2 (1)	C1-C2-C3	120 (1)
S3-Mo2-S4	70.8 (1)	C1-C2-C4	121 (1)
S1-Mo1-O1	110.5 (3)	C7-C6-C8	119 (1)
S2-Mo1-O1	108.2 (3)	C3-C2-C4	126.8 (9)
S5-Mo1-O1	106.0 (3)	C6-C8-N4	178 (2)
S6-Mo1-O1	106.4 (3)	C6-C7-N3	178 (2)
S1-Mo2-O2	109.5 (3)	C2-C4-N2	179 (2)
S2-Mo2-O2	109.8 (3)	C2-C3-N1	179 (2)
S3-Mo2-O2	104.8 (3)	Mo1-S5-C5	89.2 (4)
S4-Mo2-O2	105.0 (3)	Mo1-S6-C5	89.3 (4)
Mo2-Mo1-O1	108.1 (2)	Mo2-S3-C1	88.4 (4)
Mo1-Mo2-O2	108.7 (2)	Mo2-S4-C1	89.2 (4)

Table V. Bond Distances (Å) in the $[NC_{16}H_{36}]^+$ Ions

N5-C9	1.51 (1)	N6-C25	1.50 (1)
N5-C13	1.49 (1)	N6-C29	1.51 (1)
N5-C17	1.50 (1)	N6-C33	1.52 (1)
N5-C21	1.52 (1)	N6-C37	1.52 (1)
C9-C10	1.52 (2)	C25-C26	1.50 (1)
C10-C11	1.54 (2)	C26-C27	1.54 (2)
C11-C12	1.46 (2)	C27-C28	1.51 (2)
C13-C14	1.49 (2)	C29-C30	1.51 (1)
C14-C15	1.53 (2)	C30-C31	1.53 (1)
C15-C16	1.51 (2)	C31-C32	1.53 (2)
C17-C18	1.49 (2)	C33-C34	1.49 (1)
C18-C19	1.55 (2)	C34-C35	1.53 (2)
C19-C20	1.44 (2)	C35-C36	1.51 (2)
C21-C22	1.51 (2)	C37-C38	1.50 (1)
C22-C23	1.54 (2)	C38-C39	1.56 (2)
C23-C24	1.43 (2)	C39-C40	1.50 (2)

Table VI. Bond Angles (deg) in the $[NC_{16}H_{36}]^+$ Ions

C9-N5-C13	113.4 (8)	C25-N6-C29	106.6 (7)
C9-N5-C17	110.5 (7)	C25-N6-C33	110.8 (7)
C9-N5-C21	105.8 (7)	C25-N6-C37	111.4 (7)
C13-N5-C17	105.6 (7)	C29-N6-C33	110.3 (7)
C13-N5-C21	111.1 (7)	C29-N6-C37	112.1 (7)
C17-N5-C21	110.4 (7)	C33-N6-C37	105.7 (7)
N5-C9-C10	115 (1)	N6-C25-C26	117.0 (8)
C9-C10-C11	111 (1)	C25-C26-C27	111.3 (9)
C10-C11-C12	117 (2)	C26-C27-C28	113 (1)
N5-C13-C14	118 (1)	N6-C29-C30	117.4 (8)
C13-C14-C15	112 (1)	C29-C30-C31	109.6 (9)
C14-C15-C16	115 (1)	C30-C31-C32	112 (1)
N5-C17-C18	117 (1)	N6-C33-C34	117.0 (8)
C17-C18-C19	112 (1)	C33-C34-C35	109.7 (9)
C18-C19-C20	115 (2)	C34-C35-C36	116 (1)
N5-C21-C22	116 (1)	N6-C37-C38	116.3 (8)
C21-C22-C23	110 (1)	C37-C38-C39	105 (1)
C22-C23-C24	114 (1)	C38-C39-C40	110 (1)

C_{2v} symmetry have been structurally characterized. The displacement of the molybdenum atom is 0.72 Å for $Mo_2S_4(S_2CN(C_4H_9)_2)_2$[9] and 0.74 Å for $Mo_2O_4(S_2CN(C_2H_5)_2)_2$.[21] These displacements are considerably larger than those found in six-coordinate sulfur or oxygen-bridged molybdenum dimers (0.30–42 Å)[6–8,17–19] but similar to the 0.75 Å observed for the monomeric complex $MoO(S_2CN(C_3H_7)_2)_2$.[20]

The Mo–Mo distance in I is 2.821 (2) Å; this compares to distances 2.80–2.92 Å for other di-μ-sulfido molybdenum[1,2,5–8] dimers. The related di-μ-oxo dimer[21] has an Mo···Mo distance of 2.580 (1) Å. The increase in the Mo–Mo distance in going from the di-μ-oxo to the di-μ-sulfido species is probably due to the larger size of the sulfur atom compared to that of the oxygen.

Table VII. Equations of Least-Squares Planes in $[Mo_2O_2S_2(S_2C_4N_2)_2]^{2-}$

Atom	Dist from plane, Å	Atom	Dist from plane, Å
Plane 1: $-0.3784X + 0.7963Y - 0.4719Z - 0.6022 = 0$			
C5	−0.01 (1)	N3	−0.01 (1)
C6	−0.03 (1)	N4	0.03 (2)
C7	−0.01 (1)	S5	0.044 (4)
C8	0.00 (2)	S6	−0.026 (4)
Plane 2: $0.3394X + 0.4998Y - 0.7968Z - 4.299 = 0$			
C1	−0.15 (1)	N1	0.14 (2)
C2	−0.04 (1)	N2	−0.04 (1)
C3	0.04 (2)	S3	−0.105 (2)
C4	−0.06 (1)	S4	0.217 (2)
Plane 3: $0.2178X + 0.5121Y - 0.8308Z - 3.9825 = 0$			
S1	−0.001 (3)	S4	−0.001 (3)
S2	0.001 (4)	Mo2	−0.71
S3	0.001 (3)		
Plane 4: $-0.2493X + 0.7441Y - 0.6198Z - 2.002 = 0$			
S1	0.019 (3)	S6	0.024 (4)
S2	−0.019 (3)	Mo1	−0.73
S5	−0.024 (4)		

The average Mo–S_b bond distance of I is 2.296 (3) Å. This compares with Mo–S_b distances between 2.294 and 2.342 Å in other systems (Table VIII). The average Mo–S(*i*-mnt) distance is 2.434 (3) Å. The structures of the cysteine[7] and cysteine methyl ester[5] complexes of the $Mo_2O_2S_2^{2+}$ core show Mo–S(cys) distances of 2.50 and 2.38 Å, respectively.

The average Mo–O distance of 1.663 (5) Å is on the short end of reported Mo–O_t distances which range from 1.66 to 1.78 Å (Table VIII). A Mo–O_t distance of 1.66 Å has also been observed for the square-pyramidal Mo(IV) complex[20] $MoO(S_2CN(C_3H_7)_2)_2$. For two di-μ-sulfido-bridged dimeric complexes Mo–O_t distances differing by 0.13 Å have been reported.[5,7] However, the estimated standard deviations for the latter two structures are 0.03 Å or greater. The present high-resolution structure of I shows two identical Mo–O_t distances (1.661 (7) and 1.667 (7) Å). It would seem tenuous to attach chemical significance to the previously reported[5,7] differences in Mo–O_t distances.

Table VIII also lists important bond distances and angles for structurally characterized di-μ-sulfido-bridged Mo(V) dimers. The S_b–Mo–S_b angle in I is 101.6 (1)° which compares to the range 101.8–104° found in other dimers. The Mo–S_b–Mo angle of 75.8 (10)° in I is in the range 74.8–77.3° found for other dimers. The Mo–S_b distances are always significantly shorter than the Mo–S_l distances as has been discussed previously.[2]

It is apparent from Figure 2 that the $Mo_2O_2S_2^{2+}$ core of I adopts cis-bent geometry (**1a**). The dihedral angle between the two $Mo(S_b)_2$ planes is 153.1°, similar to that observed for other di-μ-sulfido-bridged dimers with cis-bent geometry (Table VIII). On the other hand, two organometallic compounds, $Mo_2O_2S_2(C_5H_5)_2$ and $Mo_2S_2(NC(CH_3)_3)_2(C_5H_5)_2$, contain trans-planar (**1b**) cores.[1,2] Both **1a** and **1b** have Mo···Mo distances which are significantly shorter than an Mo–Mo single bond (3.12 Å in $Mo_2(CO)_{10}^{2-}$),[22] and compounds of both geometries are diamagnetic at room temperature.

The statistically significant differences in Mo···Mo distances and in the dihedral angles between $Mo(S_b)_2$ planes for structures **1a** and **1b** have been previously noted but not explained.[2] We suggest that geometries **1a** and **1b** can be understood by considering the steric requirements for fusion of two hypothetical monomeric $MoO(S_b)_2L$ fragments (here L is $C_5H_5^-$ or $S_2C_2(CN)_2^{2-}$). There are two ways in which these monomeric fragments can be joined by sharing S atoms as shown in Figure 3. In I the steric requirements of the *i*-mnt

Table VIII. Important Distances and Angles for $Mo_2O_2S_2^{2+}$ Compounds[a]

Compd	Mo· · ·Mo, Å	Mo-O_t, Å	Mo-S_b, Å	Mo-S_l, Å	Mo-S_b-Mo, deg	S_b-Mo-S_b, deg	Core geometry	Dihedral angle,[b] deg	Ref
$[(n\text{-}C_4H_9)_4N]_2[Mo_2O_2S_2(i\text{-mnt})_2]$	2.821 (2)	1.664 (7)	2.300 (4)	2.434 (3)	75.8 (1)	101.6 (1)	cb	153.1	This work
$Mo_2O_2S_2(SCH_2CH(NH_2)CO_2CH_3)_2$	2.804 (4)	1.65 (3) 1.78 (3)	2.31 (1)	2.38 (1)	74.8 (4)	101.8 (5)	cb	149.1	5
$Na_2[Mo_2O_2S_2(SCH_2(NH_2)CO_2)_2]$	2.82	1.55 1.69	2.33	2.50	75	103	cb	156	7
$Cs_2[Mo_2O_2S_2(EDTA)]$	2.779 (1)	1.683 (6)	2.294 (1)		75.2 (1)	102.1 (1)	cb	152.3	8
$Mo_2O_2S_2(NHCHNCHCCH_2(NH_2)CO_2)_2$	2.82 (1)	1.71 (2)	2.32 (2)		74.9 (5)	104.0 (5)	cb	153	6
$MoO_2S_2(C_5H_5)_2$	2.894 (5)	1.679 (6)	2.317 (3)		77.3 (1)	102.7 (1)	tp	180	1
$Mo_2(NC(CH_3)_3)_2S_2(C_5H_5)_2$[c]	2.920 (1)		2.342 (1)		77.14 (3)	102.86 (4)	tp	180	2
$Mo_2S_4(S_2CN(C_4H_9)_2)_2$[d]	2.801 (2)		2.307 (3)	2.447 (5)	74.7 (1)	101.8 (7)	cb	148.1	9

[a] O_t = terminal O, S_b = bridging S, S_l = S from ligand, cb = cis bent, tp = trans planar. [b] Angle between the two $Mo(S_b)_2$ planes. [c] Contains terminal $NC(CH_3)_3$ groups rather than O_t. [d] Contains S_t rather than O_t.

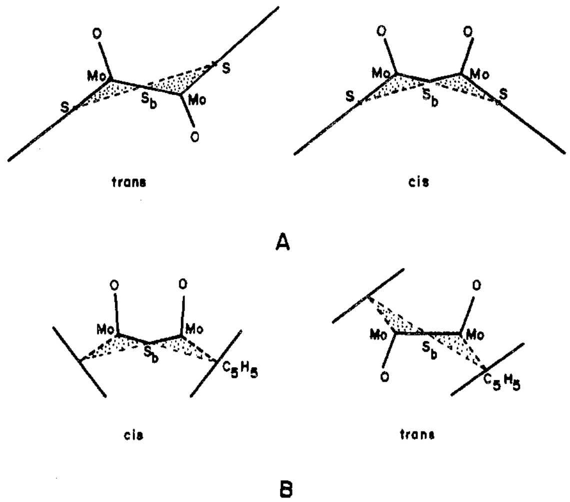


Figure 3. (A) Projections of the structure of the $[Mo_2O_2S_2(i\text{-mnt})_2]^{2-}$ ion along the $S_b\cdot\cdot\cdot S_b$ vector showing the trans (hypothetical) and cis (observed) geometries. (B) Projections of the structure of $Mo_2O_2S_2(C_5H_5)_2$ along the $S_b\cdot\cdot\cdot S_b$ vector showing the cis (hypothetical) and trans (observed) geometries.

ligands appear similar for cis and trans fusion. Steric interaction of the O atoms is not important in I because the O1···O2 distance (3.87 Å) is much greater than the van der Waals contact (2.8 Å).[23] The observed cis-bent geometry minimizes the Mo···Mo distance which should maximize any direct interaction between the Mo atoms. For $Mo_2O_2S_2(C_5H_5)_2$, however, the steric interactions between the C_5H_5 rings will be minimized by the observed trans fusion. Additional studies of $Mo_2O_2S_2L_2$ complexes are needed to verify the importance of simple steric considerations for determining cis-bent and trans-planar geometries.

The *i*-mnt ligands are both planar. The equations for the least-squares planes along with the displacements of each atom out of the plane are given in Talbe VII. The bond distances and bond angles do not deviate significantly from those in coordinated 1,2-dicyanoethylene-1,2-dithiolate.[24-26] The two tetra-*n*-butylammonium ions have normal bond lengths and angles (Tables V and VI).

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Supplementary Material Available: Listings of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Molecular Geometry of $HRu_3(CO)_{10}(C{=}NMe_2)$, Including the Direct Location of the μ_2-Bridging Hydride Ligand

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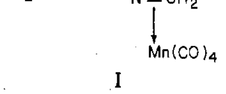
The trinuclear complex $HRu_3(CO)_{10}(C{=}NMe_2)$, previously prepared from the reaction of $Ru_3(CO)_{12}$ and $(Me_2NCH_2)SnMe_3$, has been characterized both by mass spectrometry and by a complete three-dimensional x-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.3171\ (9)$ Å, $b = 35.8137\ (35)$ Å, $c = 11.9616\ (10)$ Å, $\beta = 97.06\ (1)°$, $V = 3961.1\ (6)$ Å^3, and $\rho(\text{calcd}) = 2.147$ g cm^{-3} for mol wt 640.41 and $Z = 8$. Diffraction data were collected with a Picker FACS-1 diffractometer, using Mo Kα radiation. The structure was solved by symbolic addition and was refined by difference-Fourier and least-squares refinement techniques. All atoms, including all hydrogen atoms, have been located, the final discrepancy indices being $R_F = 2.41\%$ and $R_{wF} = 3.45\%$ for the 3702 reliable independent reflections with $2\theta < 40°$. There are two crystallographically independent molecules within the asymmetric unit; a comparison of bond distances and angles within these two molecules shows excellent agreement, average disagreements between "equivalent" values being 0.004 Å for Ru–Ru, 0.011 Å for Ru–CO, 0.012 Å for Ru–$CNMe_2$, 0.009 Å for C–O, and 0.007 Å for N–C distances. Each molecule has approximate C_s symmetry and contains a triangular arrangement of ruthenium atoms, one of which is linked to four terminal carbonyl ligands and two of which are linked to three terminal carbonyl ligands. The two $Ru(CO)_3$ groups are linked by a bridging hydride and a bridging $Me_2N^+{=}C^-$ ligand and are associated with Ru–Ru distances of 2.7997 (5) Å [molecule 1] and 2.8016 (6) Å [molecule 2] as compared to nonbridged $(OC)_4Ru{-}Ru(CO)_3$ bonds of length 2.8216 (6)–2.8336 (6) Å. Ruthenium–hydrogen bond distances are Ru(11)–H(1) = 1.93 (5) Å and Ru(12)–H(1) = 1.85 (5) Å (in molecule 1) and Ru(21)–H(2) = 1.80 (3) Å and Ru(22)–H(2) = 1.82 (3) Å (in molecule 2); Ru–H–Ru angles are 95 (2) and 101 (2)°, respectively. The results of this structural study, taken in conjunction with available crystallographic information on other systems containing bridging hydride ligands, are used in assessing the effects of bridging hydride ligands on metal–metal distances.

Introduction

The fission reactions of organotin amines,[3] sulfides,[4] and allyls[5] with transition metal halides have led to a number of unusual transition metal complexes. Recently, Abel and co-workers have examined the reaction of metal carbonyl halides with (dialkylaminomethyl)trialkyltin [$R_2NCH_2SnMe_3$] complexes and have demonstrated[6,7] that species containing η^2-bonded dialkylaminomethylene ligands are produced; a crystal structure determination[6] of (aziridinylmethylene)tetracarbonylmanganese (I) has confirmed this unequivocally.



I

Abel and Rowley recently found[8] that (dimethylaminomethyl)trimethyltin reacts with triruthenium dodecacarbonyl to yield the known species $(Me_3Sn)_2Ru(CO)_4$ and a new triruthenium cluster complex for which no unique formulation was, at the time, possible. We have undertaken a single-crystal x-ray diffraction study of this latter species and found it to be $HRu_3(CO)_{10}(C{=}NMe_2)$ (vide infra). A preliminary account of this work appeared earlier.[9]

Experimental Section

(A) Collection of the X-Ray Diffraction Data. A crystalline sample of the complex was provided by Professor E. W. Abel of the University of Exeter, Exeter, England. The crystals form characteristic orange hexagonal plates and decompose upon exposure to air for prolonged periods. The crystal selected for the diffraction experiment was a hexagonal plate between {010} faces 0.15 mm apart, bounded by {101}, {2$\bar{1}$0}, and {03$\bar{2}$}; the plate face was of maximum dimensions 0.55 mm × 0.40 mm. The crystal was mounted along its extended a direction by glueing it with General Electric "Glyptal" to the tip of a thin glass fiber which was fixed into a brass pin using beeswax and mounted on a eucentric goniometer head. The crystal was subsequently protected from air by coating it with a thin film of shellac.

Preliminary Weissenberg, rotation, precession, and cone-axis photographs yielded approximate cell dimensions, indicated C_{2h} $(2/m)$ Laue symmetry, and revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ is thus indicated. [$P2_1/n$ is a nonstandard setting of space group $P2_1/c$ (C_{2h}^5; No. 14) having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.]

The crystal was transferred to a Picker FACS-1 automated diffractometer, was accurately centered, and was oriented in a random orientation with a^* offset by 2.17° from the instrumental ϕ axis. Unit cell measurement and data collection were carried out as described